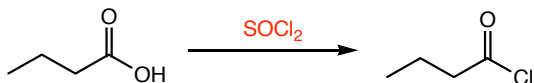


## Chem. 218 Problem Set 10

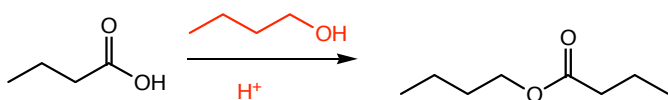
Recommended Problems from the book: 22.4-22.5, 22.10-22.31, 22.42-22.50, 22.53-22.57, 22.58, 22.60-22.64, 22.66-22.69, 22.85-22.86, 28.13-28.15, 28.19-28.20, 28.53-28.60.

(1<sup>st</sup> ed: 22.5-22.6, 22.11-22.31, 22.41-22.51, 22.53-22.57, 22.59, 22.61-22.69, 22.84-22.85, 28.13-28.15, 28.19-28.20, 28.52-28.59.)

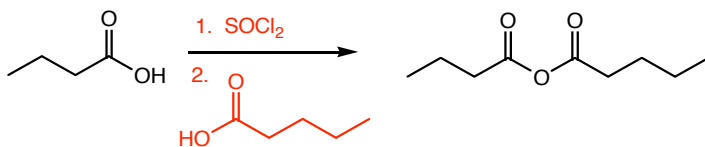
a.



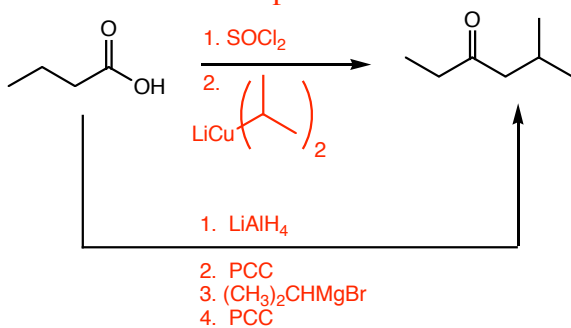
b.



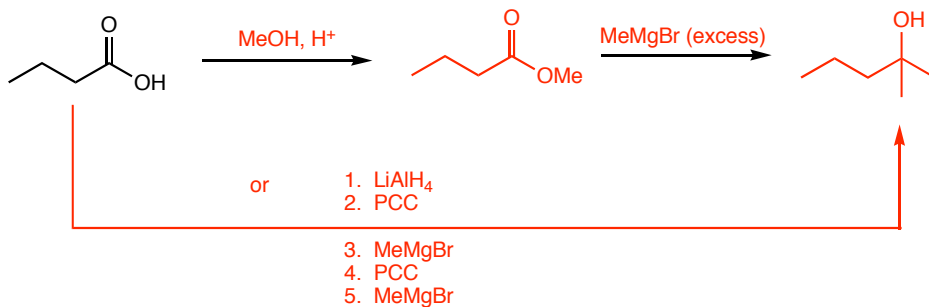
c.



d. Here are two possibilities:

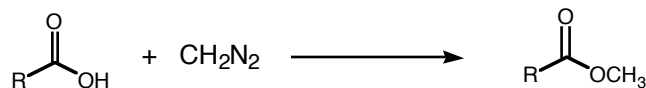


e.





4. One frequently used method for preparing methyl esters is by reaction of carboxylic acids with diazomethane,  $\text{CH}_2\text{N}_2$ :



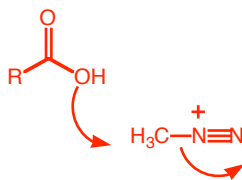
The reaction occurs in two steps: (1) protonation of diazomethane by the carboxylic acid to give the diazonium ion  $\text{CH}_3\text{N}_2^+$  plus a carboxylate anion, and (2), reaction of the carboxylate with the diazonium ion.

(a) Draw two resonance structures of diazomethane to account for step 1.

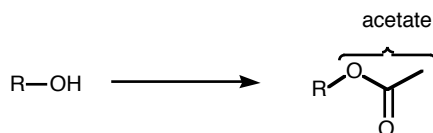


(b) What kind of reaction occurs in step 2?

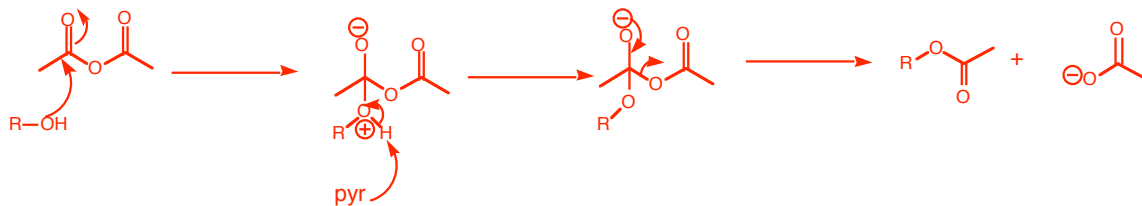
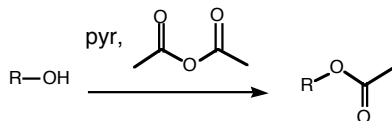
$\text{S}_{\text{N}}2$ :



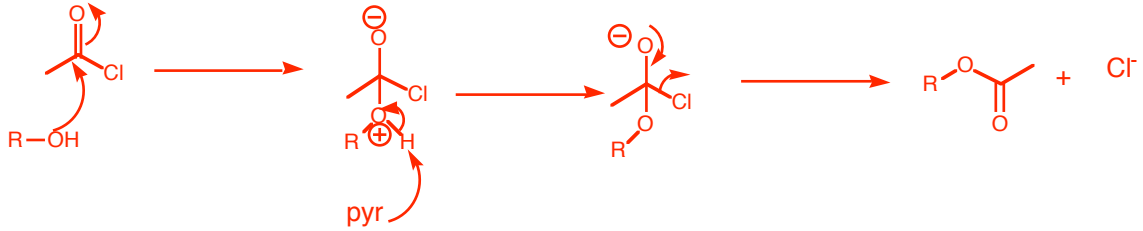
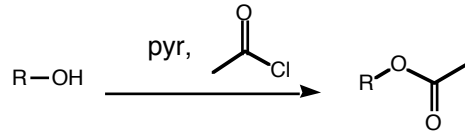
5. Acetate groups are commonly used as protecting groups for alcohols. The following methods have all been used to install an acetate protecting group on an alcohol. Draw all of the products that are formed in addition to the acetate, and draw the mechanism for each reaction.



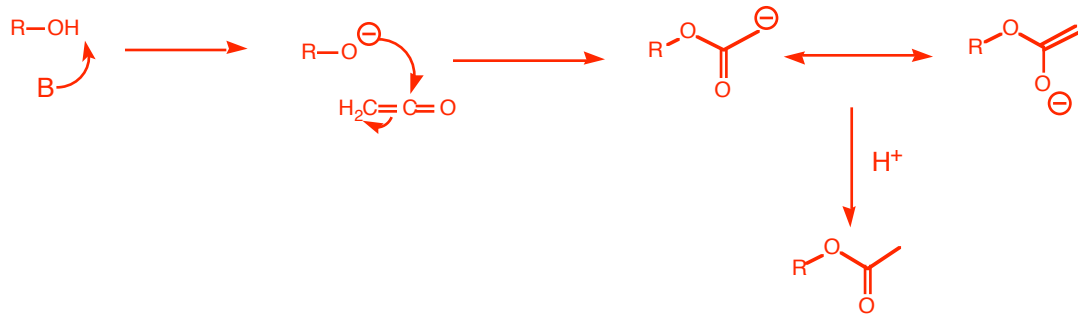
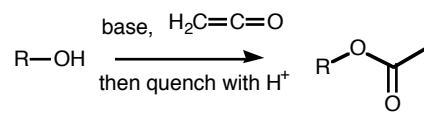
(a)



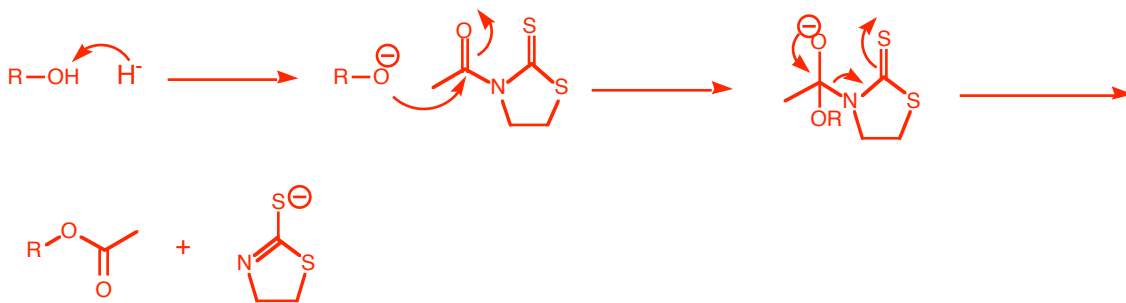
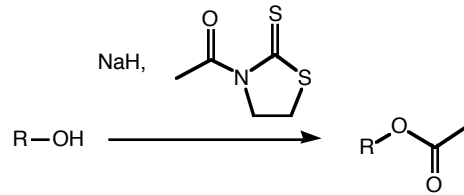
(b)



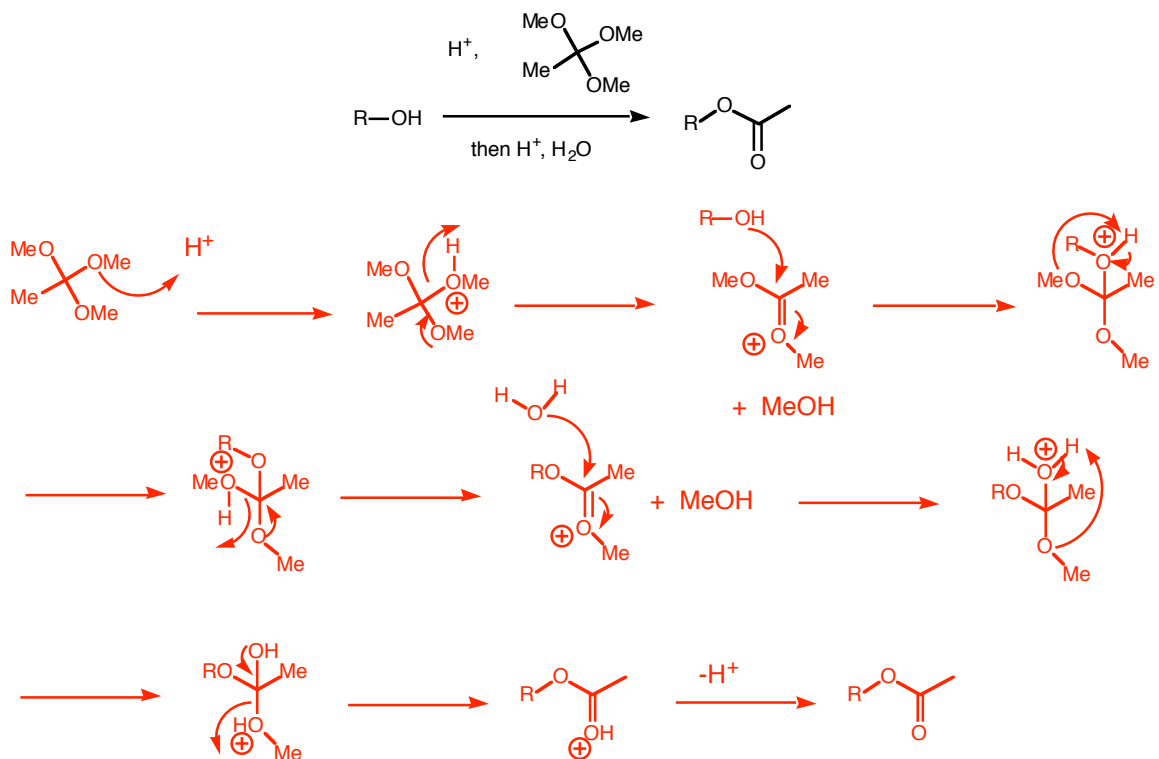
(c)



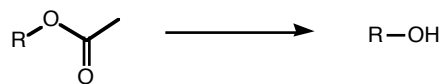
(d)



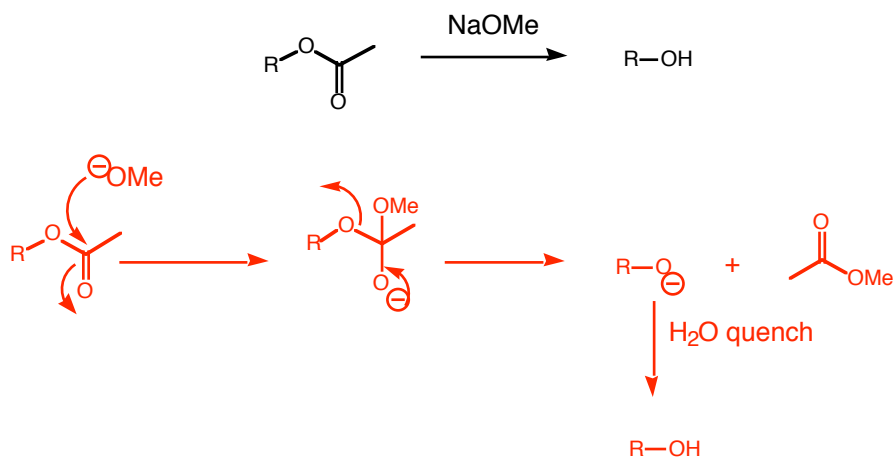
(e)



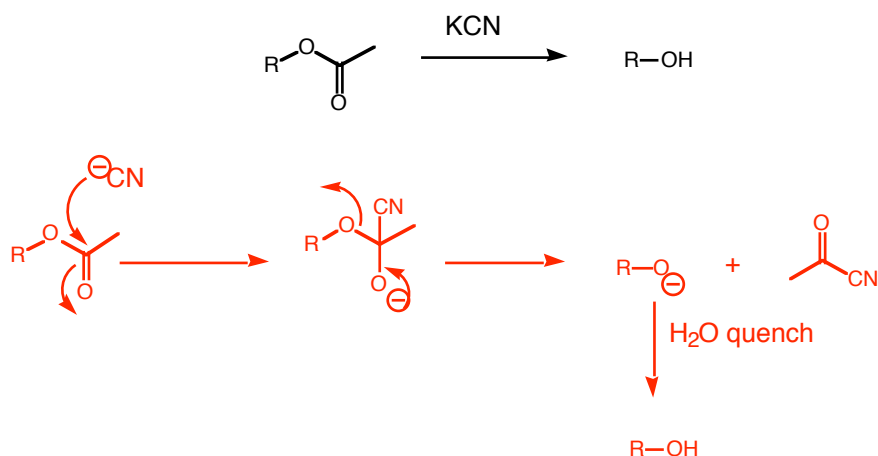
6. The following methods have been used to remove acetate protecting groups. Draw all of the products and mechanism for each reaction.



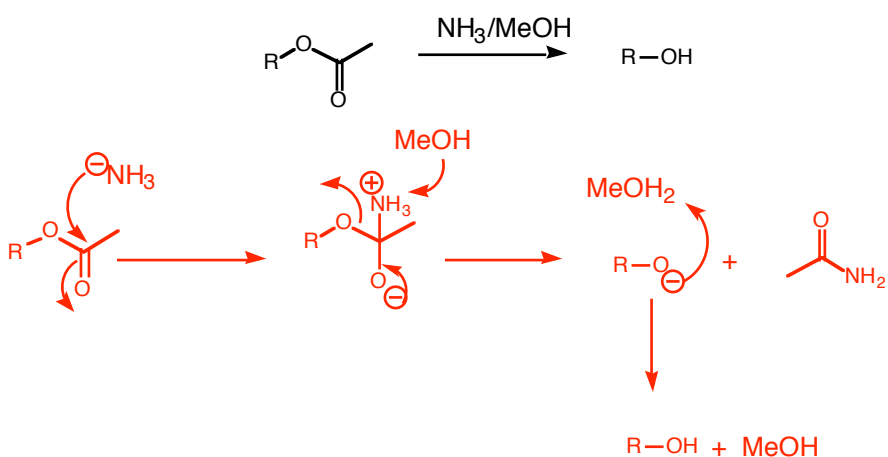
(a)



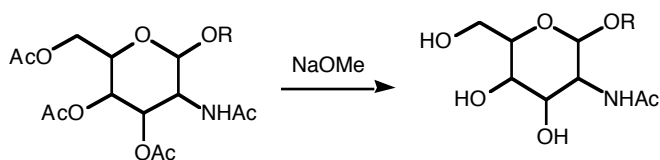
(b) KCN



(c)

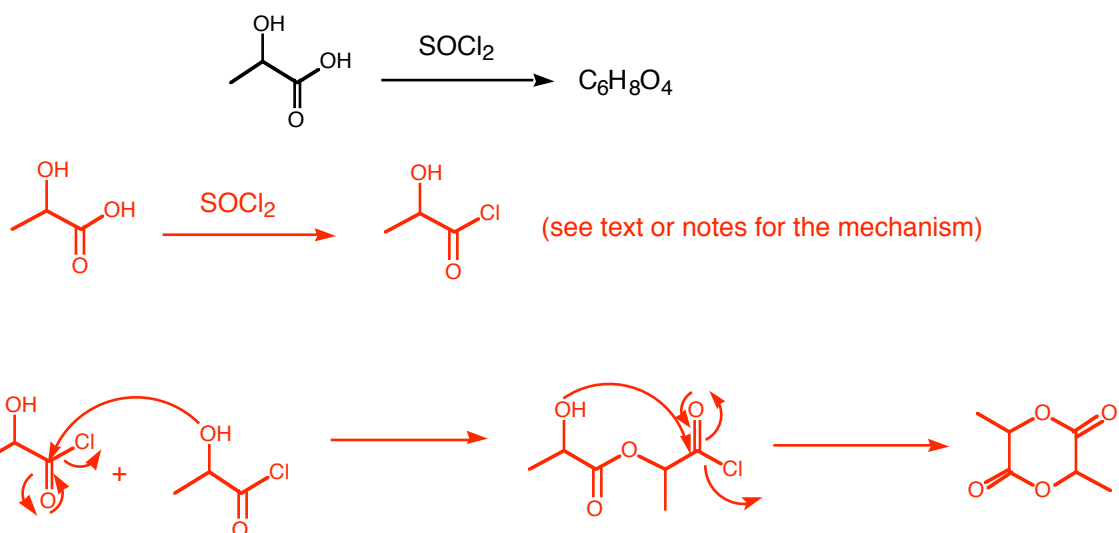


7. It is possible to remove an acetate protecting group from an alcohol in the presence of an amine. Explain why.

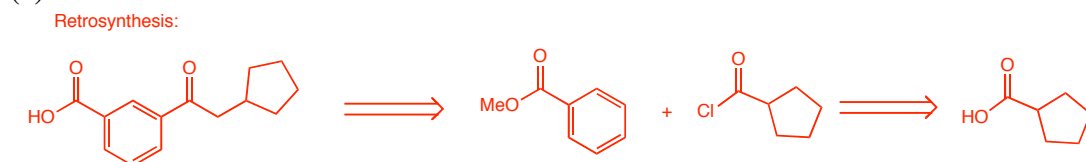
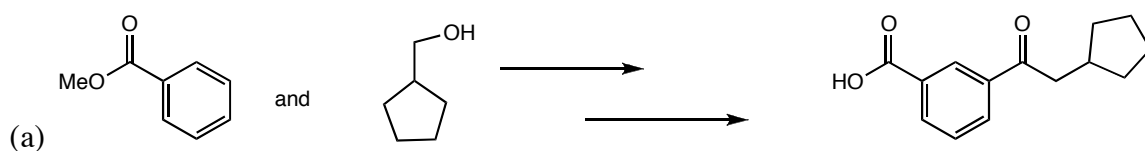


Amides are much more stable than esters, so they are much less reactive to nucleophiles such as methoxide.

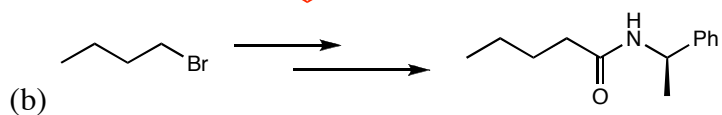
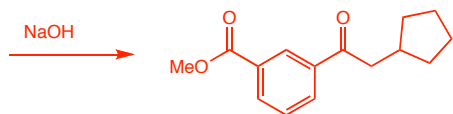
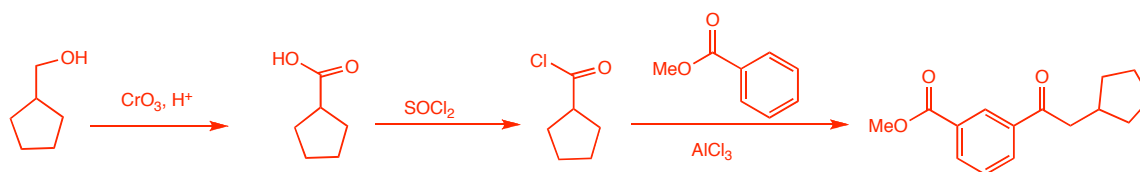
8. When lactic acid (2-hydroxypropanoic acid) is heated with one equivalent of thionyl chloride, a product with MF  $\text{C}_6\text{H}_8\text{O}_4$  is formed. Draw the product and the mechanism for its formation. Hint: it is cyclic.

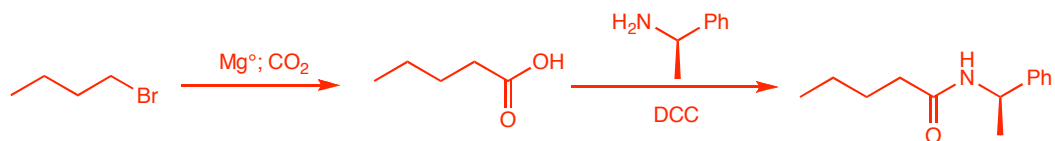
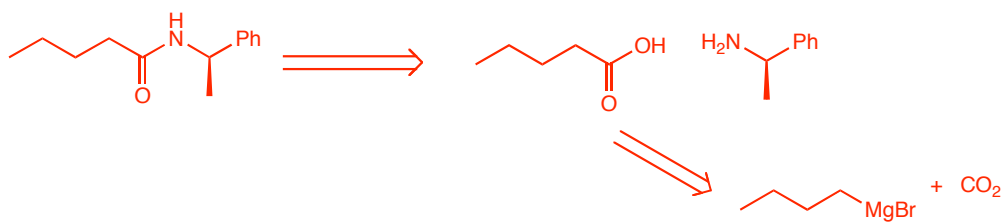


9. Propose a synthesis of the following molecule using the starting materials given:

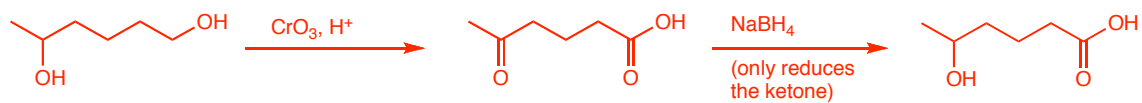
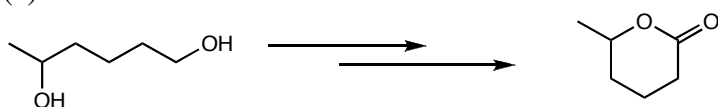


Forward:

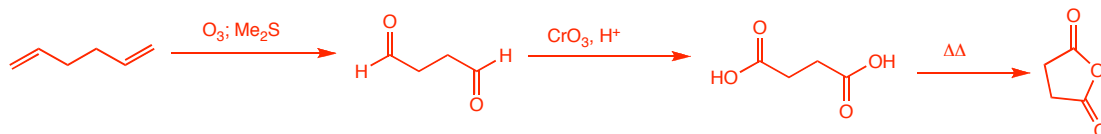
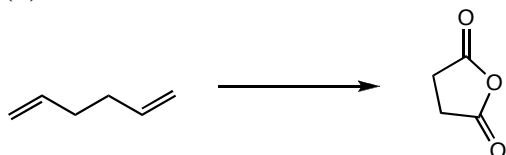




(c)



(d)



(e)

